

AD-A196 946

REPORT DOCUMENTATION PAGE

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			1b. RESTRICTIVE MARKINGS	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N00014-86-K-0428-43			3. DISTRIBUTION / AVAILABILITY OF REPORT Unrestricted	
6a. NAME OF PERFORMING ORGANIZATION University of Illinois Department of Chemistry	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Chemistry Division		
6c. ADDRESS (City, State, and ZIP Code) 1209 W. California St. Urbana, IL 61801		7b. ADDRESS (City, State, and ZIP Code) Arlington, Virginia 22217-5000		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-86-K-0428		
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
		WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) Photoreduction of Substituted Arenes with Borates and Borohydride: An Electron Transfer Mechanism				
12. PERSONAL AUTHOR(S) Schuster, Gary B.; Kropp, Michael				
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM 1/86 TO 1/87	14. DATE OF REPORT (Year, Month, Day) July 6, 1988	15. PAGE COUNT 6	
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
			Photo-dehalogenation, aromatic hydrocarbons , Electron transfer reaction.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)				
Electronically excited aryl nitriles and halides react with borohydride or with alkyl borates by an electron transfer reaction path to give reduction products. (Kropp)				
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL Gary B. Schuster			22b. TELEPHONE (Include Area Code) 217-333-0695	22c. OFFICE SYMBOL

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OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0428

R&T Code 413a001

Technical Report No. 43

Photoreduction of Substituted Arenes with Borates and Borohydride:
An Electron Transfer Mechanism

by

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Prepared for Publication

in

Tetrahedron Letters

University of Illinois
Department of Chemistry
Urbana, IL

July 6, 1988



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PHOTOREDUCTION OF SUBSTITUTED ARENES WITH BORATES AND BOROHYDRIDE:
 AN ELECTRON TRANSFER MECHANISM

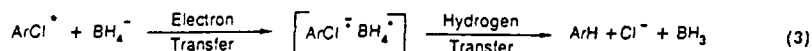
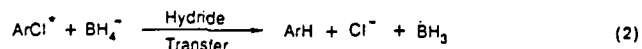
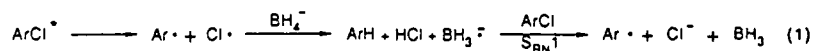
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Summary: Electronically excited aryl nitriles and halides react with borohydride or with alkyl borates by an electron transfer reaction path to give reduction products.

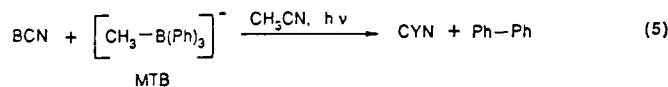
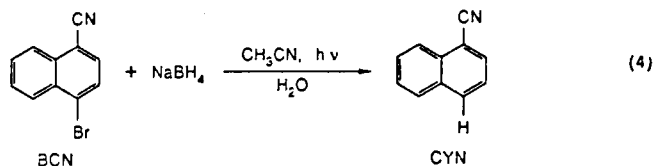
The photoreduction of organic compounds with inorganic metal hydrides is a topic of long-standing interest and recently recognized importance. Early, pioneering work by Pashovitch,¹ Barltrop,² Letsinger³ and Onishi⁴ showed that the irradiation of aromatic hydrocarbons, nitriles, nitro compounds, or halides in the presence of NaBH₄ gives products from formal substitution of hydride onto the aromatic nucleus. More recently, Epling and Florio re-examined these reactions and established relative rates for a group of related aryl chlorides,^{5a} and Abeywickrema and Beckwith reported photo-dehalogenation of arenes in the presence of NaBH₄ and di-tert-butyl peroxide.^{5b}

There is considerable interest in defining the mechanism for photoreduction of arenes by NaBH₄. Three pathways have been advanced that are supported by experimental observations. In all cases the reaction is initiated with the excitation of the arene by absorption of light. In the first postulate (eq 1), the excited arene undergoes bond homolysis to form an aryl radical and a halogen atom. These radicals abstract hydrogen atoms from BH₄⁻ giving BH₃⁻, which initiates an S_{RN}1-like⁶ chain reaction to form the observed products. Alternatively, it has been proposed that in some cases the excited arene itself reacts directly with BH₄⁻ either by a direct hydride transfer process (eq 2) or by a single electron transfer-hydrogen atom transfer sequence (eq 3) to give the isolated products.



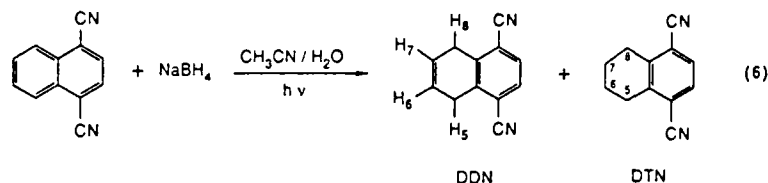
We report herein investigation of the reduction of electronically excited arenes by NaBH_4 and by alkyl(triphenyl)borates $[\text{R}(\text{Ph})_3\text{B}]^-$. Analysis of these reactions with isotope tracer techniques and by laser transient absorption spectroscopic methods supports the single electron transfer hypothesis.

Irradiation (350 nm, Rayonet Reactor) of 1-bromo-4-cyanonaphthalene⁷ (BCN, 0.011 M) in acetonitrile/water (9/1; v/v) containing NaBH_4 (0.06 M) gives exclusively 1-cyanonaphthalene (CYN) in 96% yield, eq 4. Irradiation of BCN under these conditions without added NaBH_4 causes no reaction; BCN is recovered unchanged in 93% yield. Similarly, there is no reaction between BCN and NaBH_4 in the absence of light. Deuterium is not significantly incorporated in the CYN when the photoreduction with NaBH_4 is carried out in $\text{CD}_3\text{CN}/\text{D}_2\text{O}$. But the CYN formed by irradiation of BCN in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ containing NaBD_4 is primarily mono-deuterated (determined by mass spectrometric analysis). The photoreduction reaction is slowed but not stopped when acrylonitrile (0.03 M), a free-radical chain inhibitor,² is added to the reaction mixture before irradiation. Precisely analogous results are obtained when these experiments are repeated with 1-chloro-4-cyanonaphthalene (CCN).



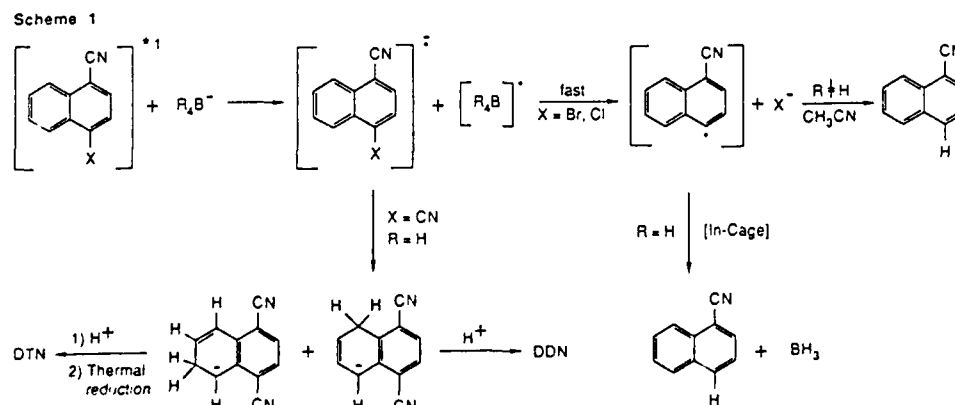
We have shown recently that organoborates function as one-electron donors in their reactions with electronically excited cyanoarenes.⁸ Irradiation of an acetonitrile solution of BCN containing methyl(triphenyl)borate (MTB, as its tetramethylammonium salt, 0.01 M) gives CYN and biphenyl (the latter from oxidation of MTB),⁹ eq 5. Significantly, when this reaction is carried out in CD_3CN solution, the CYN formed is mono-deuterated. The same results are obtained when tetraphenylborate is the electron donor or when the arene is CCN.

Irradiation of a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution of 1,4-dicyanonaphthalene (DCN) in the presence of NaBH_4 gives 1,4-dicyano-5,8-dihydronaphthalene (DDN) and 1,4-dicyano-5,6,7,8-tetrahydronaphthalene (DTN) in nearly quantitative overall yield (DDN : DTN ca. 3:1), eq 6.¹⁰ Both DDN and DTN are primary photochemical products; DDN is not converted to DTN by irradiation, and their yield ratio is constant throughout the reaction. When this experiment is repeated with NaBD_4 , the DDN contains one deuterium at position 5 and DTN is dideuterated with one deuterium at position 5 and one at position 7 (the extent and position of deuteration was determined by $^1\text{H-NMR}$ spectroscopy). Irradiation of DCN in a $\text{CH}_3\text{CN}/\text{D}_2\text{O}$ solution containing NaBD_4 gives dideuterated DDN (positions 5 and 8) and tetradeuterated DTN (positions 5, 6, 7 and 8).



The radical anion of DCN is readily observed with transient absorption techniques on a nanosecond timescale.¹¹ Pulsed laser irradiation (337 nm, 13 ns, 7 mJ) of DCN in an acetonitrile/water solution containing naphthalene as an electron donor gives a transient species absorbing strongly at 390 nm. This spectrum is identical with the one assigned to DCN^{•-}, previously in a related experiment run with MTB as electron donor in the absence of water.⁸ When the laser absorption experiment is repeated with NaBH₄ as donor instead of naphthalene, the DCN radical anion can not be observed, but a puny absorption at 440 nm assigned to residual triplet DCN is detected.

These experiments provide information about the mechanism of the photoreduction of arenes with borates and borohydrides. The findings are consistent with a general scheme whose specific outcome is determined by the exact nature of the reagents, Scheme 1. In all cases, the excited singlet state of the arene reacts by accepting an electron from the borate or the borohydride. This is the predicted outcome from the usual Weller treatment since ΔG_{ET} is negative for all these reactions.¹² The radical anion of BCN or CCN formed in this reaction (i.e. X = Br or Cl) dissociates rapidly to form the halide ion and the cyanonaphthyl radical. This process is well-precedented in the electrochemistry of related species¹³ and evidently occurs on too fast a time scale to permit detection of the radical anion by nanosecond laser techniques. When the electron donor is borohydride (R = H), the cyanonaphthyl radical rapidly abstracts a hydrogen atom from the borohydranyl radical [$\text{BH}_4\cdot$] to form CYN and (presumably) BH₃. When the electron donor is a borate, the boranyl radical [$\text{R}_4\text{B}\cdot$] does not contain an easily transferable hydrogen atom, and the cyanonaphthyl radical abstracts a hydrogen atom from the solvent.



The reaction follows a modified course when $X = CN$ (i.e. DCN). The DCN radical anion formed in the electron transfer step does not fragment to the cyanonaphthyl radical. When borohydride ($R = H$) is the electron donor, a hydrogen is transferred from the borohydryl radical to either the 5- or the 6 position of the DCN radical anion. The first option gives DDN after protonation, the second choice gives DTN after protonation and a second (presumed thermal) reduction. This general sequence was considered earlier and ruled out because the products do not correspond to those obtained in the classical Birch reduction, which also proceeds through a radical anion intermediate.² However in the photoreduction, transfer of the hydrogen atom to the radical anion occurs before it is reduced a second time to a dianion (as it is under Birch conditions), and thus no similarity in the products obtained should necessarily be expected.

In sum, the chemical and spectroscopic evidence reported herein supports a sequential electron-hydrogen atom transfer mechanism for photoreduction of the examined cyano-substituted arenes by organoborates. By analogy, the related reductions of other arenes by $NaBH_4$ may follow the same route if energetically permitted ($\Delta G_{ET} < 0$). This offers the interesting prospect of a general reaction procedure to give products unobtainable by conventional, thermal routes.

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DTN: ¹H-NMR (CDCl₃) δ 7.53 (s, 2H), 2.99 (m, 4H), 1.87 (m, 4H).
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Acknowledgments: This work was supported in part by a grant from the National Science Foundation and in part by a grant from The Office of Naval Research.

(Received in USA 1 July 1987)